Effect of position of electron acceptor group substitution on NLO properties of chalcones derivatives: A DFT study

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Abstract- In the present work the effectiveness of the substitution of electron acceptors on the nonlinear optical activity of D-π-A-π-A system has been studied to understand origin of nonlinear optical effect and also the structure-property relationship. The computational study was carried out using Density Functional Theory (DFT) by employing B3LYP/6-31G(d) level of theory. The ground state dipole moments (μ) and first static hyperpolarizability (β) were computed at the same level of theory. To understand and to optimize NLO property the electron acceptor group substitution on the para-position of phenyl group has been varied. Also the effectiveness of the position of functional group substitution on the NLO effect has been discussed based on the computational results. To understand the mode of charge transfer FMO analysis was carried out. Among the selected molecular structures, system with nitro group at para-substitution exhibits higher value of β. From the HOMO-LUMO study it is clear that there exists a strong intramolecular charge transfer from donor to acceptor through the π-conjugation system. The computational results suggest that system 4 can be a potential material for the NLO applications.

Key words—DFT, hyperpolarizability, Nonlinear optics (NLO), organic materials

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1 INTRODUCTION

Photonics has become a prominent field wherein a variety of potential Nonlinear Optical (NLO) materials are being used for photonic applications such as electro optics, optical switching, optical data storage, biological species detection, remote sensing etc. [1-5]. In order to have better NLO properties the tuning of the microscopic NLO properties are very essential. One may obtain high NLO properties by substituting a strong electron donor and an electron acceptor at the ends of the molecules by keeping the π-conjugate bridge of sufficient length. Such molecules are of the push-pull category with D-π-A type structure [6-7]. The problem with these classes of materials is that as one increases the donor/acceptor strength the dipole moment also tend to increase resulting in molecular dipole-dipole interactions. Such an interaction usually results in anti-parallel alignment of molecular dipole in crystal structure. Such an arrangement of molecular dipole is disadvantageous due to decreased SHG efficiency or centrosymmetric structure of such molecular crystals. Moreover the design of NLO material for specific NLO applications is a challenging task. Therefore the design and selection of organic molecular material plays a crucial role in NLO. Organic molecules are emerging as better candidates in the field of NLO due its structural diversity, ease of synthesis, thermal and chemical stability, high NLO coefficient etc. [8-10]. Among the organic molecules for NLO applications chalcones are the class of organic system with high NLO efficiency, efficient intermolecular charge transfer ability, wider optical transparency and good crystallizability [11].

In order to enhance the NLO properties a proper combination of donors/acceptors groups and a π-conjugation bridge are essential [13-14]. Thus we have different type of π-conjugated system such as D-π-A, D-π-A-π-D and D-π-A-π-A. In the present study to understand the effect of acceptor substitution on different position of phenyl ring and electron accepting strength on the NLO properties and also to explore the structure-property relation in such π-conjugated system the Density Functional Theoretical (DFT) studies have been carried out on selected molecules and the results obtained are discussed in this article.

2 Computational details

All the quantum chemical calculations were performed using Gaussian03 program package [14]. DFT computational studies have been extensively used as a tool to understand the molecular structure-properties relationship as the results computed using DFT methods are in close agreement with the experimental results. The designed molecular structures were optimized by employing density functional Becke3-Lee Yang-Parr (DFT/B3LYP) level of theory with 6-31G(d) basis set. Gauss View5.0 [15] was used for the visualisation and interpretation of the results.

The electronic dipole moment and static first hyperpolarizability were computed. The molecular dipole moment is calculated by the following equation

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2) \qquad (1)$$

The average polarizability (α_o) is defined as per the equation

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$$\alpha_o=(\alpha_{xx}+ \alpha_{yy}+ \alpha_{zz})^{(1/3)} \quad (2)$$

The static first hyperpolarizability (β_{tot}) is calculated by making use of the following equation

$$\beta_{tot}=(\beta_x^2+ \beta_y^2+ \beta_z^2)^{1/2} \quad (3)$$

where $\beta_x= \beta_{xxx}+ \beta_{xyy}+ \beta_{xzz}$

$\beta_y= \beta_{yyy}+ \beta_{xxy} +\beta_{yzz}$

$\beta_z= \beta_{zzz}+ \beta_{xxz}+ \beta_{yyz}$

In general the first hyperpolarizability β is a third rank tensor defined with 3x3x3 matrix. But according to Kleinmann symmetry the 27 components of the matrix reduce to 10 components.

3 Results and Discussions

In order to study the effect of different electron acceptor groups and also to understand the structure-property relationship in D-π-A-π-A system, electron donor (amino) group at para position of carbonyl phenyl group was fixed and the electron acceptors of different strength at para-position of phenyl group present at other end of the molecule was varied. To optimize NLO effect the positions of the electron acceptor group was changed and the computational study on the effect of electron acceptor group substitution at different positions on phenyl ring was carried out. Based on the above design criteria the geometrical structures of **system 1**, **system 2**, **system 3** and **system 4** with IUPAC names (2*E*)-1-(4-aminophenyl)-3-(4-bromophenyl)prop-2-en-1-one, 4-[(1*E*)-3-(4-aminophenyl)-3-oxoprop-1-en-1-yl]benzonitrile, 4-[(1*E*)-3-(4-aminophenyl)-3-oxoprop-1-en-1-yl]benzaldehyde, and (2*E*)-1-(4-aminophenyl)-3-(4-nitrophenyl)prop-2-en-1-one, respectively are designed with different electron withdrawing groups namely Br, CHO, CN and NO_2. All the designed molecular structures were optimized and NLO properties were computed using density functional theory by adopting B3LYP functional with the basis set 6-31G(d). In order to understand the effectiveness of the position of electron acceptor group on the NLO property two more structures are designed with NO_2 group at ortho and meta positions and are named as system 4a and 4b [(2*E*)-1-(4-aminophenyl)-3-(2-nitrophenyl)prop-2-en-1-one, (2*E*)-1-(4-aminophenyl)-3-(3-nitrophenyl)prop-2-en-1-one)], respectively. The optimized structures are shown in Fig.1

The computed results of the molecular structures are listed in Table1. System 4 with nitro group substituted at para position shows larger value of dipole moment. The strong push pull configuration based on the electron donor and electron acceptors at the ends of molecular system attributes for the higher value for the dipole moment. System 4 exhibited larger value of β (65.6x10^{-30}esu) which is 130 times that of standard urea.

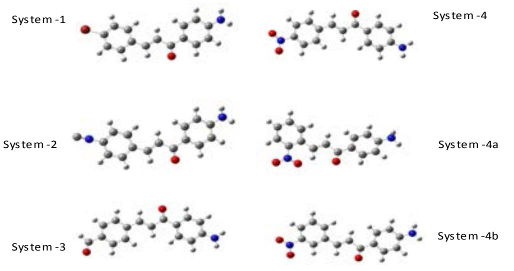

Fig.1 Optimized structures of designed molecules

The first static hyperpolarizabilities were calculated by taking into account of different components of β as per equation (3). The calculated β values are found to follow the variation as system 1< system 2 < system 3 < system 4. Based on the inductive effect possessed by the different acceptor groups it was expected that the β value of molecular system with CN substitution ie system 3 should have smaller value when compared to CHO substituted system. But the computational results show that system 2 is having smaller value of β in comparison with system 3. The charge distribution on the carbon atom attached to CHO group is having a charge of 0.100 a.u. where as in system 2 the carbon atom attached with CN is showing a value of 0.290a.u.Thus the extent of charge transfer to the acceptor side is found to be more effective in System 3 compared to System 2. As per the computational study, System 4 exhibits better NLO activity compared to other compounds. To understand the effectiveness of the position of electron acceptor groups on the NLO activity, the first static hyperpolarizability values, for NO_2 group at ortho and meta positions are also been computed and are listed in Table 2. The molecular system with NO_2 at para-position found to exhibit higher first static hyperpolarizability value which is almost twice as that of System 4a and 4b.

Structures	**Dipole moment (Debye)**	**First static hyperpolarizability(10^{-30}esu)**
System 1	1.856	19.1
System 2	2.5	32.5
System 3	2.86	47.8
System 4	3.019	65.6

Table 1: The calculated ground state dipole moment (μ) and first static hyperpolarizability (β) calculated at B3LYP/ 6-31G(d) level of theory

The plot of hyperpolarizability β with respect to electron acceptors with different electron acceptor strength is shown in Fig.2

	System 4a	System 4b	System 4
β_{xxx}(esu)	-3859.76	-3823.18	-6985.4
β_{xxy}(esu)	-851.9	-1461.7	1376.16
β_{xyy}(esu)	-55.28	-87.25	-476.65
β_{yyy}(esu)	-144.76	112.82	53.53
β_{xxz}(esu)	649.1	62.53	48.03
β_{xyz}(esu)	17.23	20.09	-22.22
β_{yyz}(esu)	-86.5	10.17	20.34
β_{xzz}(esu)	-71.99	4.18	2.79
β_{yzz}(esu)	4.65	4.96	-4.67
β_{zzz}(esu)	-26.15	0.58	1.1
β_{tot}(esu)	**35.8x10^{-30}**	**35.7x10^{-30}**	**65.6x10^{-30}**

Table 2: The calculated first static hyperpolarizability (β) values for system 4, 4a and 4b.

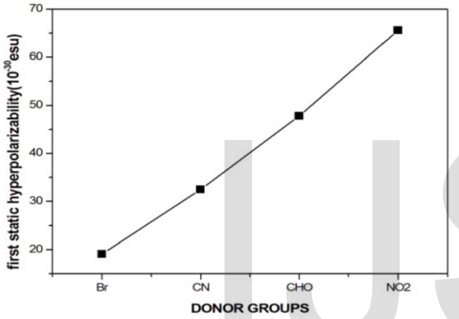

Fig 2. Variation of first static hyperpolarizability with the substitution of various electron acceptors.

Frontier Molecular Orbital(FMO) Analysis

To understand the NLO behaviour of the designed structures HOMO-LUMO study was carried out. Intramolecular charge tranfer is very well understood by the the analysis of FMOs at HOMO and LUMO. The 3D plots of FMO at highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for the designed molecules are shown in the Fig.3. The energies in the HOMO and LUMO levels are listed in Table 3. By comparing the difference in the HOMO - LUMO it is clear that the system with the nitro group at para position shows least value for the energy gap. As the gap between the energy levels decreases the charge transfer becomes easier. Thus explaing the larger value of hyperpolarizability of the order 65.6x10^{-30}esu. It can be seen that in HOMO the charge density is spread over benzene ring which is attched with the amino group. In LUMO the charge distribution has been shifted over the benzene ring attached to nitro group.Thus there is an intramolecular charge transfer in the designed system wherein the amino group acts as a electron donor and nitro group acts as an electron acceptor. Generally carbonyl group acts as an electron withdrawing group. Thus the system possess D-π-A-π-A type push-pull system (or effective D-π-A system).

structure	HOMO(a.u)	LUMO(a.u)	ΔE(a.u)
System 4	-0.218	-0.102	0.116
System 3	-0.215	-0.089	0.126
System 2	-0.215	-0.083	0.132
System 1	-0.212	-0.073	0.139

Table 3: Energy values at HOMO-LUMO(a.u)

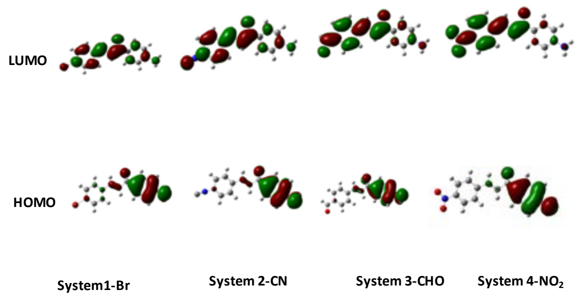

Fig 3. Frontier molecular orbitals of the molecular systems 1, 2, 3 and 4

4 Conclusion

The position and substitutional effect of groups with different electron withdrawing strength on NLO property was studied through the theoretical approach. Among the selected electron acceptor groups Br,CHO,NO$_2$ and CN system with the substitution of nitro group at the para postion exhibited larger value for β of 65.6x10^{-30}esu which is 130 times that of standard urea. From the FMO anlalysis it is clear that there is an intramolecular charge transfer between the donor and acceptors. By considering the amino group as an electron donor which is at one end of the molecular system and different substitutional groups as the electron acceptors it can be conclude that the designed structures belongs to D-π-A-π-A system or it can be also called as effective D-π-A system.

ACKNOWLEDGMENT

The authors thank Prof. Swapan K. Pati, JNCASR for allowing to run the G03 programs in their cluster. HJR thanks DAE-BRNS, Govt. of India (2012/34/18/BRNS/871) and VGST (GRD-451) for the research grant. The authors also thank the principal and Management for the support.

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